Degradation of plastic carrier bags in the marine environment

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ABSTRACT

There is considerable concern about the hazards that plastic debris presents to wildlife. Use of polymers that degrade more quickly than conventional plastics presents a possible solution to this problem. Here we investigate breakdown of two oxo-biodegradable plastics, compostable plastic and standard polyethylene in the marine environment. Tensile strength of all materials decreased during exposure, but at different rates. Compostable plastic disappeared from our test rig between 16 and 24 weeks whereas approximately 98% of the other plastics remained after 40 weeks. Some plastics require UV light to degrade. Transmittance of UV through oxo-biodegradable and standard polyethylene decreased as a consequence of fouling such that these materials received ~90% less UV light after 40 weeks. Our data indicate that compostable plastics may degrade relatively quickly compared to oxo-biodegradable and conventional plastics. While degradable polymers offer waste management solutions, there are limitations to their effectiveness in reducing hazards associated with plastic debris.

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1. Introduction

Production of plastic has increased from 0.5 million tonnes in 1950 to 260 million tonnes in 2007 (Plastic Europe, 2008). This increase in usage, especially disposable items of packaging, which make up 37% of all the plastic produced (Plastic Europe, 2008), has created waste management issues with end of life plastics accumulating in landfill and in natural habitats (Thompson et al., 2009a). Such debris is particularly evident in marine environments where items of plastic have been reported from the poles to the equator, with 60–80 percent of marine litter being plastic (Derraik, 2002). The substantial quantity of marine plastic debris and its durability creates physical hazards for wildlife which may ingest or become entangled in this debris (Derraik, 2002; Gregory, 2009). In addition, there is evidence that ingestion of plastic debris may also present a threat as chemicals including phthalates, PCB's and organochlorine pesticides, either added during manufacture or absorbed from seawater have been reported on plastic fragments (Andrady et al., 1993; Teuten et al., 2009; Mato et al., 2001) and may present a toxicological hazard (Teuten et al., 2007). Conventional plastics show high resistance to aging and minimal biological degradation. When plastics are exposed to UVB radiation in sunlight and the oxidative and hydrolytic properties of the atmosphere and seawater, respectively, polymers can be oxidized, forming hydroperoxides which lead to polymer chain scission (Billingham et al., 2000). However, these would require further degradation before they would become bio-available. The miner-

alisation rate from long-term biodegradation experiments of both UV-irradiated samples (Albertsson and Karlsson, 1988), non-pretreated, and additive-free low density polyethylene samples, in natural soils indicate it is likely to take more than 100 years for mineralisation of polyethylene to occur (Ohtake et al., 1998).

The present study examined the degradation of carrier bags with formulations that could reduce their persistence in the environment. These materials were compared in the marine environment, using realistic conditions that discarded carrier bags could experience.

Reduction in tensile strength and loss of surface area of plastic materials were used as standard methods to indicate degradation. Tensile elongation before breakage is a standard method used to determine the degradation end point for degradable polymers as outlined by the American Society for Testing and Materials (ASTM D3826-98 (2008)). In terms of surface area loss, the European Standard, EN13432, states that one of the characteristics that a compostable bag must show is fragmentation and loss of visibility. Considering that fragments formed during this trial would be lost to the sea during exposure, surface area remaining was used to measure visible loss of material.

The plastic materials tested included two different oxo-biodegradable formulations trademarked as TDPA™ (EPI, 2008), a biodegradable bag manufactured using GM-free corn starch, vegetable oils and compostable polyesters (BioBag, 2009) and a standard polyethylene bag produced from 33% recycled materials. TDPA™ formulations are additives that, when compounded with conventional polymers at appropriate levels are intended to alter the formation and decomposition of hydroperoxides. Their use allows control of the lifetime of plastic items while maintaining

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stability during processing, storage and short-term use. Once these materials are discarded in the environment, chemical degradation (initiated by heat, UV light or mechanical stress in the environment) may be accelerated by several orders of magnitude (EPI, 2008). Billingham et al. (2000) indicated that the oxidized molecular fragments are hydrophilic, with molar mass values reduced by a factor of 10 or more, and are ultimately biodegradable. The compostable bag used in this study was certified as such and therefore should decompose into carbon dioxide under the action of microbes with at least 90% of the organic material being converted into CO_2 within 6 months (European-Bioplastics). Monitoring the release of CO_2 is a good test for biological degradation but was not practical to use in this marine field trial. A standard polyethylene carrier bag was included in this study for comparison.

It is widely established that hard surfaces, such as plastic, will become fouled when immersed in seawater (Wahl, 1989). Fouling organisms absorb light; this is important since any reduction in light reaching the surface of the plastic would be expected to reduce rates of degradation. Hence changes in the amount of UV light reaching the surface of plastic samples was quantified.

The main aim of this study was therefore to compare the degradation rate of carrier bags with different formulations over a 40 week period in the marine environment. A second aim was to establish whether fouling by marine organisms reduced the amount of UV light reaching the surface of plastic samples.

2. Materials and methods

Four types of plastic that are used as carrier bags were compared. A d_2w and EPI polyethylene, termed oxo-biodegradable, both of which use the Totally Degradable Plastics Additives (TDPA™), the BioBag produced by the Mater-Bi company which consists of corn starch, vegetable oils and compostable esters and a standard polyethylene bag produced from 33% recycled materials. Herein these materials are described as TDPA™ 1, 2, compostable polyester and standard polyethylene.

Bags were obtained from retailers in Devon, UK, during April 2008 and cut into 7 cm by 1 cm strips. Wooden sample holders (20) were deployed with 25 strips of each type of plastic stapled to each sample holder, leaving a 4 cm by 1 cm area of plastic hanging free. Sample holders were fastened to a beam attached to a floating pontoon at Queens Anne Battery Marina, Coxside Plymouth, Devon (50° 21′57.07 N, 004° 07′55.07 W) in May 2008. Plastic bags are frequently reported floating at or near the surface but are also present at greater depths (Barnes et al., 2009). Here, the beam was deployed at 0.6 m to represent conditions near the sea surface whilst standardising the depth and exposure conditions. Samples were removed in order to examine degradation at 4, 8, 16, 24 and 40 weeks.

After removal from the field, degradation was quantified in terms of reduction in tensile strength and surface area loss. There were five replicates of each bag type at each sample time for each analysis. For surface area and tensile strength analyses any surface biofouling on the samples was removed with tissue paper. To accurately measure changes in surface area loss, plastic samples were examined using ImageJ analysis and visualisation using a camera mounted on a light microscope. Tensile strength is a standard method used to quantify degradation (ASTM D3826-98 (2008)) and the maximum extension (mm) until breakage was measured using the Universal Testing Machine (Instron 3345 – USA) at an extension rate of 15 mm per minute.

A UV spectroradiometer (Macam SR9910.V7) was used to determine the amount of UV light transmitted through the plastic together with any biofilm that had developed on its surface. Trans-

mittance was measured at 335 nm using five replicates of each plastic at each exposure period.

Data on effects of exposure period on surface area remaining and tensile strength were compared using ANOVA (GMAV 5, 1997, coded by A.J. Underwood and M.G. Chapman). A two-factor ANOVA was performed with material type and exposure time as fixed factors for tensile strength data. Two, one-factor ANOVAs were performed for surface area loss and tensile strength of compostable polyester with exposure time as the fixed factor. Homogeneity of variance of data was examined using Cochran's test. Pearson's correlation (Minitab V15) was used to examine the relationship between exposure time and UV transmittance.

3. Results

All 20 sample holders were successfully recovered from the sea. Progressive surface area loss was observed for the compostable polyester to the extent that no samples remained at 24 weeks. Biofilms were present on the surface of all samples after 4 weeks exposure and progressively increased in thickness over time with macro-fouling organisms (e.g. *Mytilus edulis*, and tunicates) being found on some samples after 8 weeks exposure.

The tensile strength of all plastic types decreased over time, but at different rates (Fig. 1). Changes in the tensile strength of compostable polyester samples could not be examined after 16 weeks due to total deterioration of those materials (Fig. 2). Therefore, two formal comparisons were made using ANOVA. The first compared changes in tensile strength for standard polyethylene, TDPA™ 1, and 2 for all exposure periods and found a significant interaction between exposure time and bag type (Table 1). A second ANOVA comparing the compostable polyester identified a significant reduction in tensile strength after 4 and 8 weeks compared with 0 week samples (Table 2).

Over the 40 week exposure period, less than 2% of surface area was lost by TDPA™ 1, 2 and standard polyethylene (Fig. 2A). Substantial progressive surface area loss was identified for compostable polyester bags up to 16 weeks, after which no samples remained (Fig. 2B). ANOVA comparing the compostable polyester found a significant loss of surface area remaining after 16 weeks exposure (*P*-value < 0.001, Table 3).

Transmittance of UV light through TDPA™ 1, 2 and standard polyethylene samples was negatively correlated with exposure period (*P* < 0.001). Such that, after 40 weeks of exposure, the surface of these plastics received approximately 90% less UV light than samples that had not been immersed in water. However, for compostable polyester, the amount of light received, only decreased by around 5% after 8 weeks exposure and was not correlated with exposure (*P* = 0.797).

4. Discussion

Here we report the degradation of several plastic materials with different compositions in the marine environment. Tensile strength of all materials decreased significantly with exposure but the extent of these changes varied among materials. Standard polyethylene showed the least reduction of tensile strength, followed by TDPA™ 1, 2 and then compostable polyester material. Over 40 weeks exposure, a 100% loss of compostable polyester material was observed while the other materials lost only approximately 2% of their surface area.

In terms of tensile strength, the greater rate of degradation for TDPA™ 1 and 2 compared with the standard polyethylene agrees with findings of Andrady et al. (1993) and Andrady (2003) who found that enhanced-photodegradable polymers disintegrated faster than conventional polymers in the marine environment. Differ-
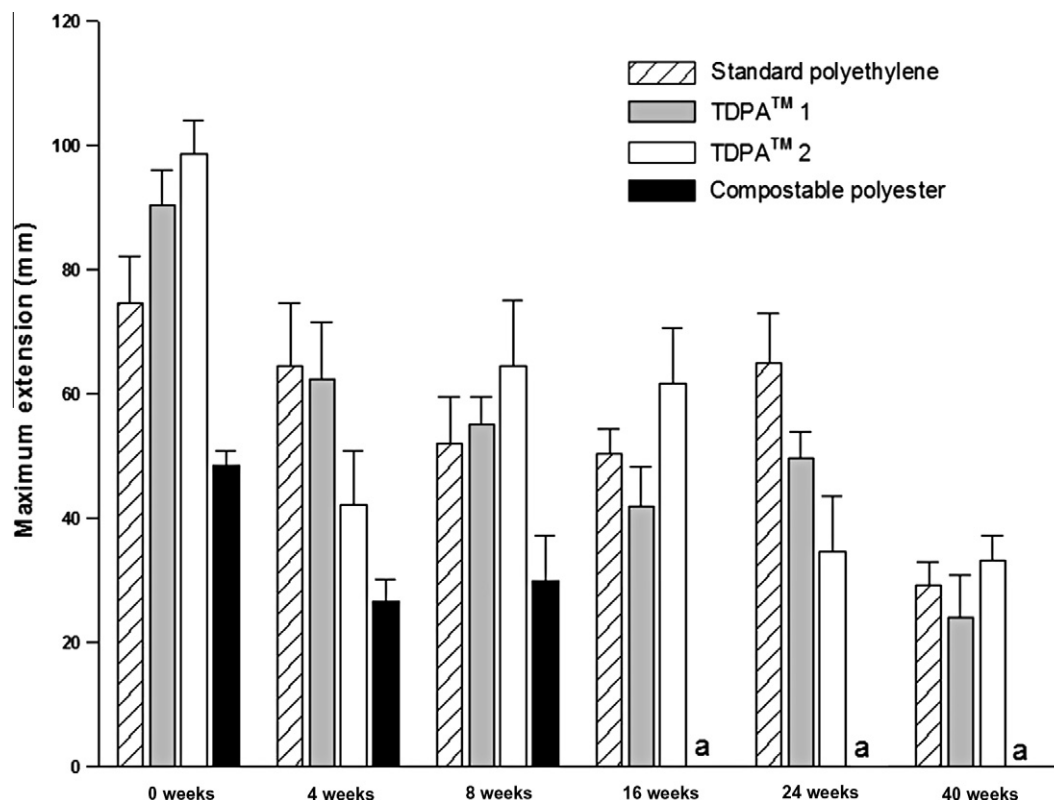
Fig. 1. Tensile strength of plastic bag samples, shown as maximum extension before breakage (mean + SE) over a 40 week exposure period in the marine environment. 'a' denotes complete degradation of compostable polyester samples. For formal comparisons see Table 1.
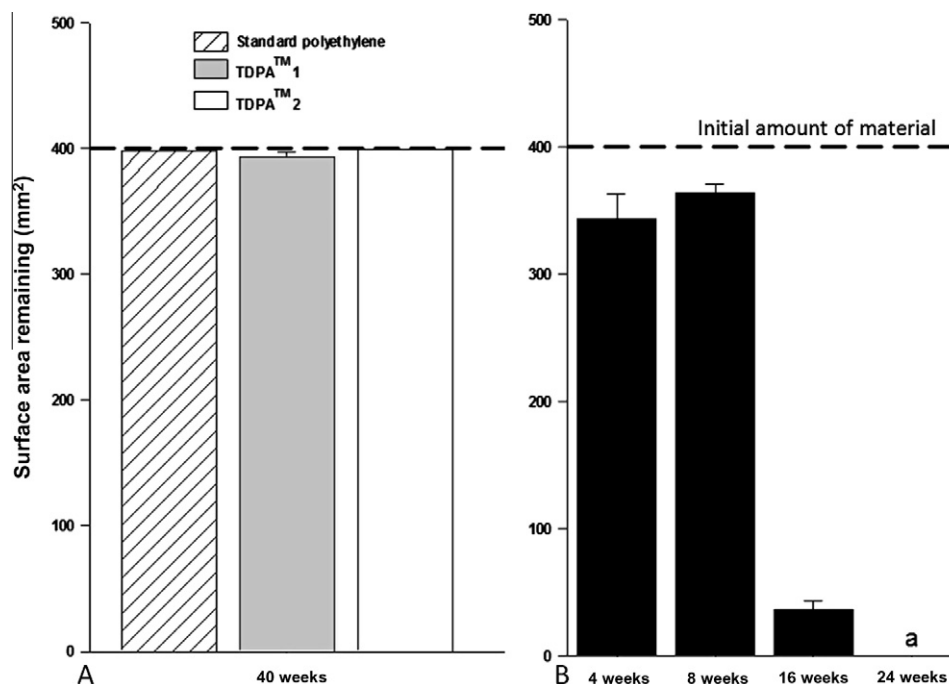

Fig. 2. Surface area remaining (mean + SE) of samples of plastic carrier bags. Dotted line indicates the initial amount of material prior to exposure. (A) Changes in surface area loss were minimal for standard polyethylene, TDPA™ 1 and 2 (<2% over time). Data for 40 weeks only are shown for brevity. (B) Compostable polyester samples showed a significant reduction in surface area remaining at 16 weeks exposure (Table 3). 'a' denotes complete absence of compostable polyester samples.

ences in the rate of degradation between TDPA™ 1 and 2 could be a result of their manufacture date. TDPA™ 1 and 2 were produced during October 2007 and February 2007, respectively. According

to the description on those bags, the degradation process should start after 18 months and complete degradation would take three years. Therefore TDPA™ 1 and 2 should have begun to degrade

Table 1
ANOVA comparing changes in tensile strength of standard polyethylene, TDPA™ 1 and 2 with exposure period displaying degrees of freedom (DF), mean squares (MS), F-statistic (F) and probability value (P-value). Post hoc SNK comparisons show the effect of exposure period varied among materials (exposure * plastic type interaction). Values underlined together indicate exposure periods that were not significantly different ($P > 0.05$).

Source	DF	MS	F	P-value
Exposure	5	5457.8	21	0.001
Plastic type	2	37.9	0.2	0.865
Exposure * plastic type	10	682.9	2.6	0.009
Residual	72	260.4		
Total	89			

SNK comparisons for exposure (weeks) * plastic type

TDPA™ 1	0 4 8 24 16 40
TDPA™ 2	0 8 16 4 24 40
Standard polyethylene	0 24 4 16 8 40

Table 2
ANOVA comparing changes in tensile strength of compostable polyester with exposure period displaying degrees of freedom (DF), mean squares (MS), F-statistic (F) and probability value (P-value). Post hoc SNK comparisons show significant effects over time. Values connected by a single line indicate exposure periods that were not significantly different ($P > 0.05$).

Source	DF	MS	F	P-value
Exposure	2	703.1	5.95	0.016
Residual	12	118.1		
Total	14			
SNK				
Exposure (weeks)	0 8 4			

Table 3
ANOVA comparing surface area remaining of compostable polyester after varying periods of exposure in the marine environment showing degrees of freedom (DF), mean squares (MS), F-statistic (F) and probability value (P-value). Post hoc SNK comparisons show significant effects over time. Values connected by a single line indicated exposure periods that were not significantly different ($P > 0.05$).

Source	DF	MS	F	P-value
Exposure	2	167811.2	211.3	0.001
Residual	12	794.1		
Total	14			
SNK				
Exposure (weeks)	8 4 16			

from April 2009 and August 2008, thus signs of deterioration should have been observed earlier in TDPA™ 2, as we reported.

The compostable polyester material degraded more than all other materials with 100% surface area loss between 16 and 24 weeks. This material was classed as a biodegradable bag (European-Bioplastics) and performed as such, exceeding the 90% reduction in biomass required after 6 months of exposure. Minimal loss of surface area for the other materials was not entirely surprising because the degradation process was expected to take longer. For TDPA™ 1 and 2, 3 years of exposure is stated by the manufacturers as the time required for complete degradation. However the efficiency of such materials as a means of reducing harm caused by marine litter is questionable if long exposures are required for degradation.

As time progressed, TDPA™ 1, 2 and standard polyethylene samples became increasingly fouled which resulted in a decline in the amount of UV light transmitted through the samples. Reduction in UV light could result in slower degradation because UV light can initiate the oxidative process, producing hydroperoxides which leads to the deterioration of plastics (Billingham et al., 2000). In addition, the reduced temperature in the marine environment has already been shown to reduce degradation of photodegradable plastics when compared to degradation in air (Andrady, 2000). Ho et al. (1999) found that the degradation rate of plastics was enhanced by an increase in temperature and relative humidity. Higher temperatures increase the rate of chemical reactions, therefore degradation of plastics (Ho et al., 1999), so variations in sea temperature are also expected to influence the degradation rate of plastics. Murata et al. (2004) suggested that with greater pressure, smaller fragments of plastic will be produced as a consequence of degradation. Therefore plastic debris found at depth could degrade faster despite such habitats being cold and dark compared to the sea surface. However, other factors are likely to have a greater affect than depth, such as the mechanical action by waves at the surface and in the littoral zone (Corcoran et al., 2009; Cooper and Corcoran, 2010). Therefore long-term studies should be conducted to confirm the period required for total degradation in a range of marine habitats. Work is also needed to confirm whether there are adverse effects from the fragmentation of plastic bags into numerous small pieces (e.g. into microplastics, Thompson et al., 2004) and to quantify any substances that are released to the environment as a consequence of this breakdown.

To gain the maximum benefit from degradable, biodegradable and compostable materials, it is essential to have clear definitions and product labelling to indicate appropriate usage and disposal of such items (Thompson et al., 2009b). A plastic carrier bag that is labelled as being 'degradable' or biodegradable is likely to be used for a single application, and could make consumers more relaxed about discarding it, rather than reusing and recycling. Some 'degradable' materials may not degrade quickly in natural habitats, with the added concern that some formulations could merely disintegrate into small pieces that are not in themselves any more degradable than conventional plastic (Barnes et al., 2009). For some biodegradable and compostable polymers, there are additional ethical issues about use of agricultural land to grow crops for production of throw away convenience items rather than for production of food (Thompson et al., 2009b). Therefore, although biodegradable polymers offer potential waste management solutions, there are limitations and considerable misunderstanding among the general public about their application (WRAP, 2007).

Acknowledgements

References

Albertsson, A.C., Karlsson, S., 1988. The three stages in degradation of polymers – polyethylene as a model substance. J. Appl. Polym. Sci. 35, 1289–1302.

Andrady, A.L., 2000. Plastics and their impacts in the marine environment. In: Proc. International Marine Debris Conference on Derelict Fishing Gear and the Ocean Environment, pp. 6–11.

Andrady, A.L., 2003. Plastics and the Environment. John Wiley and Sons, West Sussex, England.

Andrady, A.L., Pegram, J.E., Song, Y., 1993. Studies on enhanced degradable plastics. II. Weathering of enhanced photodegradable polyethylenes under marine and freshwater floating exposure. J. Environ. Polym. Degr. 1, 117–126.

Barnes, D.K.A., Galgani, F., Thompson, R.C., Barlaz, M., 2009. Accumulation and fragmentation of plastic debris in global environments. Philos. Trans. B 364, 1985.

Billingham, N.C., Wiles, D.M., Cermak, B.E., Gho, J.G., Hare, C.W.J., Tung, J.F., 2000. Controlled-lifetime environmentally degradable plastics based on conventional polymers. Addcon World, Basel (RAPRA Technology, 2000).

BioBag, 2009. Product information about Mater-Bi. BioBags (Scotland) Ltd. (Internet). Available from: <http://www.biobags.co.uk/technical/mater_bi.htm>.

Cooper, D.A., Corcoran, P.L., 2010. Effects of mechanical and chemical processes on the degradation of plastic beach debris on the island of Kauai, Hawaii. Mar. Pollut. Bull. 60, 650–654.

Corcoran, P.L., Biesinger, M.C., Grifi, M., 2009. Plastics and beaches: a degrading relationship. Mar. Pollut. Bull. 58, 80–84.

Derraik, J.G.B., 2002. The pollution of the marine environment by plastic debris: a review. Mar. Pollut. Bull. 44, 842–852.

EPI, 2008. About TDPA™ – an additive for oxo-biodegradable plastics. Available from: <http://www.epi-global.com/en/products/oxobiodegradable.htm>.

European-Bioplastics, Standard EN 13432 and EN 14995 – Proof of compostability of plastic products. Available from: <http://www.european-bioplastics.org/index.php?id=158>.

Gregory, M.R., 2009. Environmental implications of plastic debris in marine settings-entanglement, ingestion, smothering, hangers-on, hitch-hiking and alien invasions. Philos. Trans. R. Soc. B – Biol. Sci. 364, 2013–2025.

Ho, K.L.G., Pometto, A.L., Hinz, P.N., 1999. Effects of temperature and relative humidity on polylactic acid plastic degradation. J. Environ. Polym. Degr. 7, 83–92.

Mato, Y., Isobe, T., Takada, H., Kanehiro, H., Ohtake, C., Kaminumas, T., 2001. Plastic resin pellets as a transport medium for toxic chemicals in the marine environment. Environ. Sci. Technol. 35, 318–324.

Murata, K., Sato, K., Sakata, Y., 2004. Effect of pressure on thermal degradation of polyethylene. J. Anal. Appl. Pyrol. 71, 569–589.

Ohtake, Y., Kobayashi, T., Asabe, H., Murakami, N., 1998. Studies on biodegradation of LDPE: observation of LDPE films scattered in agricultural fields or in garden soil. Polym. Degrad. Stab. 60, 79–84.

Plastic Europe, 2008. The compelling facts about plastics 2007. An analysis of plastics production, demand and recovery for 2007 in Europe. Available from: <www.plasticseurope.org>.

Teuten, E.L., Rowland, S.J., Galloway, T.S., Thompson, R.C., 2007. Potential for plastics to transport hydrophobic contaminants. Environ. Sci. Technol. 41, 7759–7764.

Teuten, E.L., Saquing, J.M., Knappe, D.R.U., Barlaz, M.A., Jonsson, S., Bjorn, A., Rowland, S.J., Thompson, R.C., Galloway, T.S., Yamashita, R., et al., 2009. Transport and release of chemicals from plastics to the environment and to wildlife. Philos. Trans. R. Soc. B – Biol. Sci. 364, 2027–2045.

Thompson, R.C., Olsen, Y., Mitchell, R.P., Davis, A., Rowland, S.J., John, A.W.G., McGonigle, D., Russell, A.E., 2004. Lost at sea: where is all the plastic? Science 304, 838.

Thompson, R.C., Swan, S.H., Moore, C.J., vom Saal, F.S., 2009a. Our plastic age. Philos. Trans. R. Soc. B – Biol. Sci. 364, 1973.

Thompson, R.C., Moore, C.J., vom Saal, F.S., Swan, S.H., 2009b. Plastics, the environment and human health: current consensus and future trends. Philos. Trans. R. Soc. B – Biol. Sci. 364, 2153–2166.

Wahl, M., 1989. Marine epibiosis. I. Fouling and antifouling: some basic aspects. Marine ecology progress series. Oldendorf 58, 175–189.

WRAP, 2007. Consumer Attitudes to Biopolymers. WRAP, Banbury, UK.